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(54) Title: NOVEL SELF-ACID-DOPED HIGHLY CONDUCTING POLYTHIOPHENES

(57) Abstract

The invention relates to thiophenes bearing (ω -sulfonate)alkoxy or (ω -sulfonic acid)alkoxy groups and water-soluble polythiophenes bearing (ω -sulfonic acid)-alkoxy side-chains prepared therefrom. The invention also relates to methods for the preparation of these compounds and to antistatic coatings and EMI shieldings comprising the polythiophenes.

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Novel Self-Acid-Doped Highly Conducting Polythiophenes

The invention relates to thiophenes bearing (ω -sulfonate)alkoxy or (ω -sulfonic acid)alkoxy groups and water-soluble polythiophenes bearing (ω -sulfonic acid)alkoxy side-chains prepared therefrom. The invention also relates to methods for the preparation of these compounds and to antistatic coatings and EMI shieldings comprising the polythiophenes.

The search for processable, stable, conducting polymers has been the goal of many studies in the past few years. Many synthetic approaches have been taken but, generally, the conducting state is obtained through a partial chemical or electrochemical oxidation (so-called doping reaction) of the conjugated moieties leading to the formation of different mobile charge carriers (radical cations, dimerized radical cations and dications).

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In most cases, processability has been obtained by the introduction of large counterions (which are introduced during the oxidation process to preserve the electro-neutrality) or by the attachment of relatively flexible side chains. It is believed that these structural modifications decrease the attractive interchain interactions and introduce favorable interactions between the substituents and the solvent.

The addition of side-chains does not only allow an easier processing of some electroactive polymers, but can also modulate the electronic properties of the conjugated main chain. For instance, it has been reported that the introduction of strong electrondonating side-chains, e.g. alkoxy groups, decreases the oxidation potential of the resulting polymers, giving a better stability of the oxidized (and conducting) state.

In US-A 5,093,033 and Macromolecules 24(1991)455, poly(3-alkoxythiophene)s are disclosed, Macromolecules 26(1993)2501 teaches poly(3,3'-dialkoxy-2,2'-bithiophene)s and poly(4,4'-dialkoxy-2,2'-bithiophene)s. Poly(3,4-cycloalkoxythiophene)s

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are known from US-A 4,987,042. All these materials show high and stable electrical conductivities with low absorption in the visible range when oxidized.

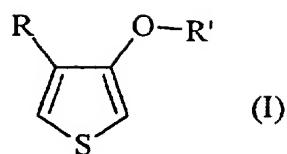
On the other hand, it has been found that the presence of different counter-ions in the doped state can significantly alter the stability of the electrical conductivity. For instance, it is believed that steric interactions between the flexible side-chains and the counter-ions are responsible for the poor stability of some of these conducting polymers, particularly at high temperatures. A partial solution to this problem was the attachment of ionic (e.g. sulfonate moieties) side-chains which allows the possibility to get the counter-ions covalently linked to the conjugated backbone (combined to a good solubility in water), leading to the concept of self-doped conducting polymers. For instance, US-A 5,367,041 discloses self-doped zwitterionic polythiophenes bearing alkylsulfonate or alkylcarboxylate side-chains.

It is worth noting that an external redox reaction must be done onto the conjugated polymer to obtain the oxidized (conducting) state but this process does not involve the introduction of any counter-ions during the doping process.

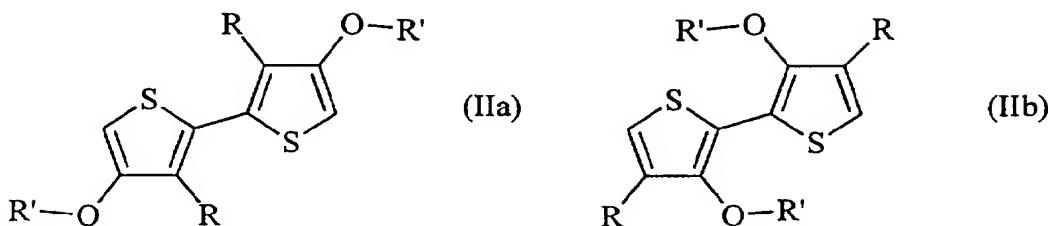
Macromolecules 26(1993)7108 and J. Chem. Soc. Chem. Commun. (1990)1694 disclose that the preparation of the acid form of sulfonated polythiophenes(involving a sulfonic acid fuctionality) is accompanied by a partial doping (oxidation) without the use of any external oxidizing agent. Thus, the presence of a strong protonic acid, oxygen (air), and a conjugated backbone can lead to conducting (doped) polymers.

Following a new synthetic approach, water-soluble polythiophenes bearing (ω -sulfonic acid)alkoxy side-chains have now been synthesized showing stable, high electrical conductivities together with low absorption in the visible range.

One aspect of the invention is to provide monomers from which such polymers can be prepared. These monomers are thiophenes corresponding to formula (I)



and bithiophenes corresponding to formulae (IIa) or (IIb)



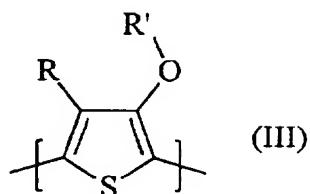
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In these formulae R represents a hydrogen atom or a C₁-C₄ alkyl group. R is preferably hydrogen or methyl, ethyl, propyl, isopropyl, butyl, isobutyl or tert.-butyl. Still more preferably R represents hydrogen or methyl in the thiophenes of formula (I) and hydrogen in the bithiophenes of formula (II), respectively.

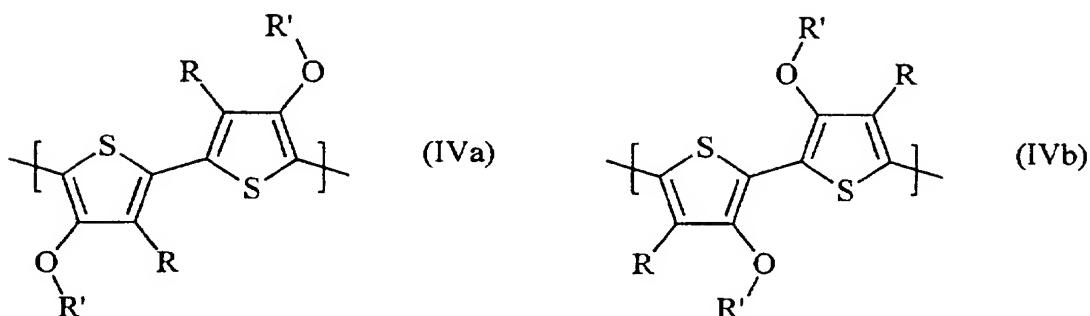
R' is -(CH₂)_n-SO₃M with n = 2 to 12, preferably n = 2, and M = H, Li, Na, K, Rb, Cs, NH₄, preferably M = Na.

Another aspect of the invention is to provide a method for the preparation of these thiophenes and bithiophenes. They can be prepared by first reacting a 3-bromothiophene, a 4,4'dibromo-2,2'-bithiophene, or a 3,3'dibromo-2,2'-bithiophene, respectively, with NaOCH₃ in the presence of CuBr to form the methoxy-substituted compound, i.e. a 3-methoxythiophene, a 4,4'-dimethoxy-2,2'-bithiophene, or a 3,3'-dimethoxy-2,2'-bithiophene, respectively. This compound is then reacted with an ω -haloalkanol HO-(CH₂)_n-X (X = Cl, Br, I, preferably X = Br; n = 2-12, preferably n = 2), in the presence of NaHSO₄. The resulting product, a 3-(ω -haloalkoxy)thiophene, a 4,4'-di(ω -haloalkoxy)-2,2'-bithiophene, or a 3,3'-di(ω -haloalkoxy)-2,2'-bithiophene, respectively, is then reacted with M₂SO₃ (M = H, Li, Na, K, Rb, Cs, NH₄, preferably M = Na, K, NH₄) to form the desired thiophene or bithiophene, respectively.

The polymers of the invention comprise recurring units of formulae (III) or (IV)



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In these formulae R represents a hydrogen atom or a C₁-C₄ alkyl group. R is preferably hydrogen or methyl, ethyl, propyl, isopropyl, butyl, isobutyl or tert.-butyl.

10 Still more preferably R represents hydrogen or methyl in the units of formula (III) and hydrogen in the units of formula (IV), respectively.

R' is $-(CH_2)_n-SO_3M$ with n = 2 to 12, preferably n = 2, and M = H, Li, Na, K, Rb, Cs, NH₄. In one preferred embodiment M is sodium, in another preferred embodiment, M is hydrogen.

The polymers of the invention can be conveniently prepared by polymerizing the thiophenes or bithiophenes in the presence of an oxidant. In most cases FeCl_3 is used for this purpose, but it is well known in the art that other oxidants can also be employed. The thiophenes or bithiophenes can also be polymerized electro-chemically.

A convenient method for obtaining the polymers in the sulfonic acid form ($M = H$) is to first polymerize a monomer bearing alkali sulfonate or ammonium sulfonate groups and then dissolve the resulting polymer in water and pass the solution through an ion-exchange resin to produce the sulfonic acid form of these polymers.

5

Alternatively, the monomer bearing the alkali sulfonate or ammonium sulfonate groups can be passed through an ion-exchange resin to produce the sulfonic acid form which can be polymerized as described above.

10 The polymers of the invention can be used as starting materials for the production of anti-static coatings or EMI shieldings. It is therefore also an aspect of the invention to provide anti-static coatings or EMI shieldings comprising the polymers of the invention. Preferably, the anti-static coatings or EMI shieldings contain the sulfonic acid form of these polymers.

15

Examples

Example 1

3-methoxy-4-methylthiophene.

22.3 g of 3-bromo-4-methylthiophene were added to a mixture of 80 mL sodium methoxide (25% in methanol), 30 mL of NMP and 11 g of CuBr. The mixture was refluxed for 3 days and after cooling, was filtrated and washed with water. The compound was extracted several times with diethyl ether. The organic phase was dried with magnesium sulfate and then evaporated. The resulting oil was purified by chromatography on a silica gel column with hexanes as eluent. Yield = 98%.

¹H-NMR (CDCl₃, ppm): 6.75 (1H, d); 6.08 (1H, d); 3.72 (3H, s); 2.04 (3H, s)

¹³C NMR (CDCl₃, ppm): 156.74; 128.53; 119.81; 95.35 56.79; 12.33

15

3-(2-bromo)ethoxy-4-methylthiophene.

4.2 g of 3-methoxy-4-methylthiophene was added to a mixture of 40 mL of toluene, 8.2 g of 2-bromo-1-ethanol (Aldrich) and 500 mg of NaHSO₄. The resulting mixture was heated until the produced methanol had been distilled off and the temperature rose to 110°C. The product was cooled and washed several times with water and, subsequently, extracted with diethyl ether. The organic phase was dried with magnesium sulfate and then evaporated. The product was purified by column chromatography using silica gel and hexanes as eluent. Yield = 55%.

¹³C NMR (CDCl_3 , ppm): 155.06; 129.18; 120.33; 97.23; 69.65; 29.20; 12.71

Sodium 3-(2-sulfonate)ethoxy-4-methylthiophene.

2.5 g of 3-(2-bromo)ethoxy-4-methylthiophene in 20 mL of acetone was added to a mixture of 1.5 g of Na₂SO₃ in 20 mL of water. The mixture was refluxed for 3 days. After cooling, the unreacted product was extracted with diethyl ether. The aqueous phase was then evaporated, giving a white crystalline powder. The desired product was recrystallized in a mixture of water/ethanol (1:1) at -10°C. Yield = 60 %.
5 M.P.: 228°C.

10 ¹H NMR (D₂O, ppm): 7.01 (1H, d); 6.51 (1H, d); 4.38 (2H, t); 3.39 (2H, t);
 2.08 (3H, s)
 ¹³C NMR (D₂O, ppm): 155.52; 130.13; 121.41; 98.92; 68.57; 50.91; 28.85;
 11.83

Example 2

15 3-(2-bromo)ethoxythiophene.
 5.00 g of 3-methoxythiophene (Aldrich) was solubilized with 11.00 g of 2-bromo-ethanol in 20 mL of toluene, then 2.00 g of NaHSO₄ was added in one portion. The mixture was heated and methanol was distilled off. The solution was cooled and
20 washed with water and diethylether. The organic phase was dried with magnesium sulfate. After evaporation, a brown liquid was obtained which was purified by column chromatography on silica gel using a mixture of CCl₄ and CHCl₃ (9:1) as the eluent. An oil was recovered which was further purified by recrystallization in methanol. White crystals were then obtained with a yield of 67%. M.P.= 46°C.

25 ¹H NMR (CDCl₃, ppm): 7.18 (1H, m); 6.78 (1H, m); 6.28 (1H, m); 4.27 (2H, t);
 3.63 (2H, t)
 ¹³C NMR (CDCl₃, ppm): 156.54; 124.79; 119.16; 98.12; 69.65; 28.62

Sodium 3-(2-sulfonate)ethoxythiophene.

To a solution of 0.48 g of Na₂SO₃ in 5.00 mL of water was added a solution of 527 mg of 3-(2-bromo)ethoxythiophene dissolved in 10 mL of acetone. The mixture was allowed to reflux for 48 hrs. The solution was then cooled and washed with diethyl ether. The aqueous phase was separated and evaporated under reduced pressure. The crude product was dissolved in water and few drops of ethanol was then added to induce the precipitation of the inorganic salt. The suspension was filtered and evaporated.

10 A white crystalline product was obtained with a yield of 37 %. This product decomposes at temperatures above 290°C before melting.

¹H NMR (D₂O, ppm): 7.46 (1H, m); 6.96 (1H, m); 6.70 (1H, m); 4.50 (2H, t);
3.47 (2H, t)

15 ¹³C NMR(D₂O, ppm): 156.96; 126.50; 120.11; 100.25; 66.25; 50.92

Example 34,4'-Dimethoxy-2,2'-bithiophene.

20 3.13 g of 4,4'-dibromo-2,2'-bithiophene was solubilized in 90 mL of sodium methoxide (25% in methanol) and 50 mL of NMP. 3.50 g of CuBr was then added in one portion and the solution was put to reflux for 24 hrs. The resulting suspension was washed with water and diethyl ether. The organic phase was separated and dried with magnesium sulfate.

25 After evaporation of the solvent, a greenish solid was obtained which was purified by chromatography on silica gel using a mixture of CCl₄ and CHCl₃ (9:1) as the eluent. A greenish solid was obtained with a yield of 37 %. M.P.: 94°C.

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¹H-NMR (CDCl₃, ppm): 6.81 (2H, d); 6.13 (2H, d); 3.79 (6H, s)

¹³C NMR (CDCl₃, ppm): 158.17; 136.07; 115.56; 95.96; 57.13

4,4'-Di(2-bromo)ethoxy-2,2'-bithiophene.

5 The product was prepared from a reaction between 529 mg of 2-bromoethanol, 1.00 g of NaHSO₄ and 236 mg of 4,4'-dimethoxy-2,2'bithiophene in 5 mL of toluene. The mixture was heated and methanol was distilled off. The solution was then cooled to room temperature and washed with water and diethyl ether. The organic portion was separated and dried with magnesium sulfate. After evaporation, a brown solution was
10 obtained which was purified by chromatography on silica gel using a mixture of CCl₄ and CHCl₃ (4:1) as the eluent. A greenish solid was obtained with a yield of 45 %.
M.P.: 171°C.

¹H NMR (CDCl₃, ppm): 6.85 (2H, d); 6.18 (2H,d); 4.27 (4H, t); 3.63 (4H, t)

15 ¹³C NMR (CDCl₃, ppm): 156.28; 136.27; 115.86; 97.79; 69.75; 28.75

Sodium 4,4'-di(2-sulfonate)ethoxy-2,2'-bithiophene.

To a solution of 390 mg of Na₂SO₃ in 4.5 mL of water was added a solution of 73.3 mg of 4,4'-diethoxy-2,2'-bithiophene dissolved in 2 mL of acetone. Then 4 mL of
20 water was added and the mixture was allowed to reflux for 48 hrs. The mixture was then washed with ether. The aqueous phase was separated and evaporated under reduced pressure. The crude product was dissolved in a mixture (1:1) of water and ethanol. The remaining inorganic salt precipitated and the suspension filtered. The aqueous phase was recovered and evaporated. A yellowish solid was obtained with a
25 yield of 50 %. This product decomposes above 290°C before melting.

¹H NMR (CDCl₃, ppm): 6.87 (2H, d); 6.40 (2H, d); 4.27 (2H, t); 3.25 (2H, t)

¹³C NMR (CDCl₃, ppm): 156.28; 136.54; 116.47; 99.82; 66.16; 50.87

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Example 4

Polymers.

1.2 g of sodium 3-(2-sulfonate)ethoxy-4-methylthiophene and 3.0 g of dry FeCl₃ were mixed in 30 mL of chloroform and stirred for 24 hrs at room temperature. The mixture was poured into 500 mL of methanol where few drops of anhydrous hydrazine have been added. After this treatment, the polymer was put in 500 mL of a 1M NaOH methanolic solution. The precipitate was filtered and a dark blue powder was obtained (yield = 50-60%).

10

Sodium poly(3-(2-sulfonate)ethoxythiophene) and sodium poly(4,4'-di(2-sulfonic acid)ethoxy-2,2'-bithiophene) have been prepared using a similar procedure. All resulting polymers showed a good solubility in water giving dark blue solutions.

15

SEC measurements revealed the polymers to have a number-average molecular weight of 6000 to 8000 with a polydispersity index of approximately 1.2.

Figures 1A to 3A show the UV-visible absorption spectra of

20

1A: Sodium poly(3-(2-sulfonate)ethoxythiophene),
2A: Sodium poly(3-(2-sulfonate)ethoxy-4-methylthiophene),
3A: Sodium poly(4,4'-di(2-sulfonate)ethoxy-2,2'-bithiophene).

25

These neutral polymers (conductivity lower than 10⁻⁵ S/cm, measured on dry pressed pellets by the four probe method) were dissolved in water and passed through an ion-exchange resin column (H⁺ type, Dowex HCR-W2), leading to the sulfonic acid form of these polymers.

30

This acid form of the substituted polythiophenes undergoes an oxidation reaction in air leading to a stable, conducting and nearly colorless state.

Figures 1B to 3B show the UV-visible absorption spectra of

1B: Poly(3-(2-sulfonic acid)ethoxythiophene),
2B: Poly(3-(2-sulfonic acid)ethoxy-4-methylthiophene),
5 3B: Poly(4,4'-di(2-sulfonic acid)ethoxy-2,2'-bithiophene).

Measurements of the electrical conductivity of the polythiophene derivatives yielded the following results:

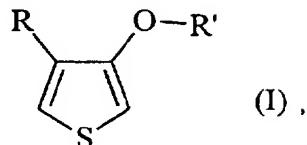
Sample	Conductivity [S/cm]
Poly(3-(2-sulfonic acid)ethoxythiophene):	0.4
Poly(3-(2-sulfonic acid)ethoxy-4-methylthiophene):	5
Poly(4,4'-di(2-sulfonic acid)ethoxy-2,2'-bithiophene):	10

10 The doping and conductivity levels found for these polythiophenes are higher than those previously reported for poly(3-(ω -sulfonic acid)alkylthiophenes), which show conductivities in the range of 10^{-2} to 10^{-1} S/cm. They also have lower oxidation potentials of 0.0 to 0.6 V vs. SCE as compared to 0.8 to 1.0 V vs. SCE for the poly(3-(ω -sulfonic acid)alkylthiophenes). The polymers show an excellent stability
15 in the acid (doped) state and no decrease of the electrical conductivity was observed as a function of time.

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Claims

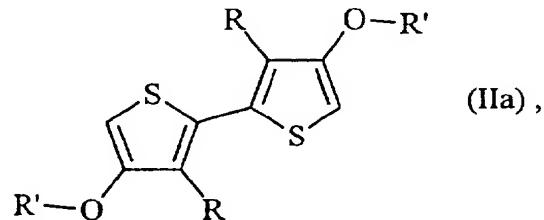
1) A thiophene corresponding to formula (I)



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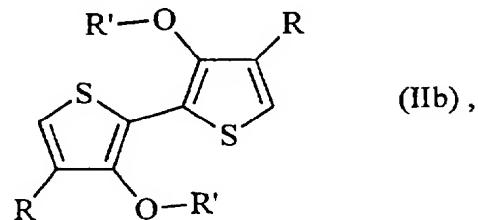
in which R is a hydrogen atom or a C₁-C₄ alkyl group and
R' is -(CH₂)_n-SO₃M with n = 2 to 12 and M = H, Li, Na, K, Rb, Cs, NH₄.

10 2) A bithiophene corresponding to formula (IIa)



15 in which R is a hydrogen atom or a C₁-C₄ alkyl group and
R' is -(CH₂)_n-SO₃M with n = 2 to 12 and M = H, Li, Na, K, Rb, Cs, NH₄.

20 3) A bithiophene corresponding to formula (IIb)



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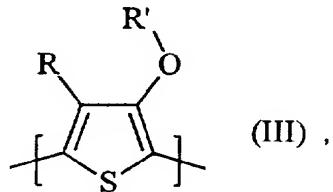
in which R is a hydrogen atom or a C₁-C₄ alkyl group and

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R' is $-(CH_2)_n-SO_3M$ with n = 2 to 12 and M = H, Li, Na, K, Rb, Cs, NH₄.

4) A polymer comprising recurring units of formula (III)

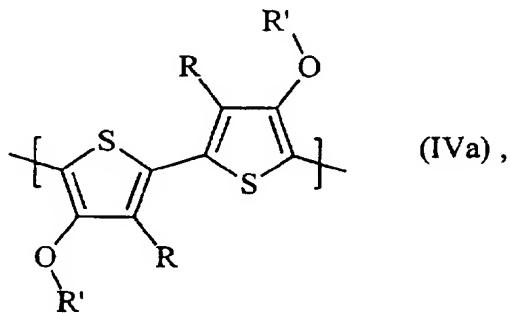
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in which R is a hydrogen atom or a C₁-C₄ alkyl group and
R' is $-(CH_2)_n-SO_3M$ with n = 2 to 12 and M = H, Li, Na, K, Rb, Cs, NH₄.

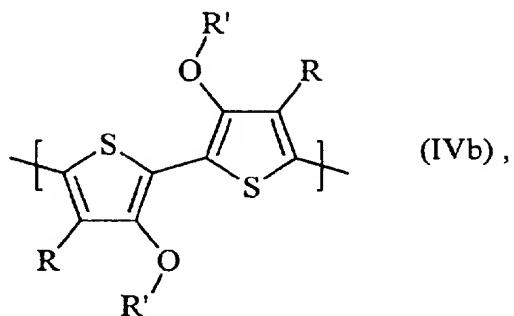
10 5) A polymer comprising recurring units of formula (IVa)

15



in which R is a hydrogen atom or a C₁-C₄ alkyl group and
R' is $-(CH_2)_n-SO_3M$ with n = 2 to 12 and M = H, Li, Na, K, Rb, Cs, NH₄.

6) A polymer comprising recurring units of formula (IVb)



5 in which R is a hydrogen atom or a C₁-C₄ alkyl group and
R' is -(CH₂)_n-SO₃M with n = 2 to 12 and M = H, Li, Na, K, Rb, Cs, NH₄.

7) A process for the preparation of the thiophene of claim 1, comprising the steps of

10 a) reacting a 3-bromothiophene with NaOCH₃ in the presence of CuBr to form a 3-methoxythiophene,
b) reacting the 3-methoxythiophene with an ω -haloalkanol in the presence of NaHSO₄ to form a 3-(ω -haloalkoxy)thiophene,
c) reacting the 3-(ω -haloalkoxy)thiophene with M₂SO₃ (M = H, Li, Na, K, Rb, Cs, NH₄) to form the thiophene of claim 1.

15 8) A process for the preparation of the bithiophene of claim 2, comprising the steps of

20 a) reacting a 4,4'-dibromo-2,2'-bithiophene with NaOCH₃ in the presence of CuBr to form a 4,4'-dimethoxy-2,2'-bithiophene,
b) reacting the 4,4'-dimethoxy-2,2'-bithiophene with an ω -haloalkanol in the presence of NaHSO₄ to form a 4,4'-di(ω -haloalkoxy)-2,2'-bithiophene,

- c) reacting the 4,4'-di(ω -haloalkoxy)-2,2'-bithiophene with M_2SO_3 ($M = H, Li, Na, K, Rb, Cs, NH_4$) to form the bithiophene of claim 2.

9) A process for the preparation of the bithiophene of claim 3, comprising the steps of

- a) reacting a 3,3'dibromo-2,2'-bithiophene with $NaOCH_3$ in the presence of $CuBr$ to form a 3,3'-dimethoxy-2,2'-bithiophene,
- b) reacting the 3,3'-dimethoxy-2,2'-bithiophene with an ω -haloalkanol in the presence of $NaHSO_4$ to form a 3,3'-di(ω -haloalkoxy)-2,2'-bithiophene,
- c) reacting the 3,3'-di(ω -haloalkoxy)-2,2'-bithiophene with M_2SO_3 ($M = H, Li, Na, K, Rb, Cs, NH_4$) to form the bithiophene of claim 3.

15 10) A process for the preparation of the polymer of claim 4 by polymerizing the thiophenes of claim 1 in the presence of an oxidant.

11) A process for the preparation of the polymer of claim 5 by polymerizing the bithiophenes of claim 2 in the presence of an oxidant.

20 12) A process for the preparation of the polymer of claim 6 by polymerizing the bithiophenes of claim 3 in the presence of an oxidant.

13) An anti-static coating or EMI shielding comprising the polymer of claim 4.

25 14) An anti-static coating or EMI shielding comprising the polymer of claim 5.

15) An anti-static coating or EMI shielding comprising the polymer of claim 6.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 97/00477

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07D333/32 C08G61/12 H01B1/12 C09D165/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07D C08G H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 253 594 A (COOKSON GROUP PLC) 20 January 1988 see abstract; claims ---	1-15
A	EP 0 257 573 A (HOECHST AG) 2 March 1988 cited in the application see abstract; claims ---	1-15
A	Y. IKENOUE ET AL.: "A Facile Preparation of a Self-doped Conducting Polymer" JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL COMMUNICATIONS, 1990, LETCHWORTH GB, pages 1694-1695, XP002041869 cited in the application see page 1694, column 2; figure 1 --- -/-	1-15

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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2

Date of the actual completion of the international search

25 September 1997

Date of mailing of the international search report

02.10.97

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Paisdor, B

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 97/00477

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 02530 A (NESTE OY ;ANDERSSON MATS (SE); OESTERHOLM JAN ERIK (FI); VAEKIPART) 3 February 1994 see abstract; claims ---	1-15
P,X	FAID K ET AL: "Functionalized regioregular polythiophenes: towards the development of biochromic sensors" CHEM. COMMUN. (CAMBRIDGE);96; (24); PP.2761-2762, UNIVERSITE DE MONTREAL;DEPARTEMENT DE CHIMIE; MONTREAL; H2M 3J7; PQ; CAN. (CA), XP002041860 see page 2762, column 1 -----	1,7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 97/00477

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0253594 A	20-01-88	AU 7571987 A EP 0253595 A JP 63107957 A JP 63045276 A US 4992559 A	21-01-88 20-01-88 12-05-88 26-02-88 12-02-91
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